

Effect of Diluents on the Curing Behavior of Vinyl Ester Resin

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ABSTRACT: An acidic vinyl ester resin (~6 mg KOH per gram of solid) was prepared by reacting a bisphenol-A-based epoxy resin with acrylic acid in the presence of tributyl amine. The acrylated epoxy resin thus obtained was characterized by Fourier transform infrared spectroscopy. Five samples of vinyl ester resin containing styrene and methyl methacrylate (MMA) in the weight ratios 40:0, 30:10, 20:20, 10:30, and 0:40 were prepared at 30°C, and their curing behavior was studied by differential scanning calorimetry in the presence of benzoyl peroxide (2 phr). Curing behavior was dependent on the ratio of the two monomers

used as reactive diluents. The kinetic parameters were determined by Ozawa's method. The energy of activation and frequency factor varied from 17 to 23 kcal mol⁻¹ and 8.47 × 10⁹ to 5.21 × 10¹² min⁻¹, respectively and were lowest for the samples containing 30:10 and 10:30 styrene/MMA weight ratios. The curing reactions followed first-order kinetics and obeyed the Arrhenius rate expression. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1948–1951, 2003

Key words: resins; curing of polymers; differential scanning calorimeter (DSC); activation energy; reaction mechanism

INTRODUCTION

Vinyl ester resins (VERs) are addition products of epoxide resins and unsaturated carboxylic acids, such as acrylic or methacrylic acids, that contain ester groups and carbon-to-carbon double-bond linkages at the end of the polymer chain. These resins can be used in neat form (i.e., no diluent) or they can contain either a vinyl-type reactive comonomer (e.g., styrene, acrylates, vinyl toluene, and trimethylolpropane triacrylate) or a nonreactive diluent (e.g.; methyl ethyl ketone or toluene).^{1,2} Undiluted VERs vary from semisolid to solid and, therefore, both the reactive and nonreactive diluents can provide workable viscosity levels. Reactive diluents are preferred because they provide systems with appropriate reactivity, viscosity, and coat-ability before cure, and desired crosslink density, chemical resistance, etc. after cure. Curing of vinyl ester is a process of free-radical copolymerization between the unsaturation of monomer/diluent and vinyl ester molecule. An understanding of cure is needed to establish the relationship between processing and properties of these resins. The cure kinetics of VERs has been studied by several investigators.^{3,4} Most of these studies have primarily been aimed at characterizing the kinetics of the curing reactions in the presence of styrene,^{5–8} substituted styrene, and

acrylates.^{9–11} However, studies related to cure kinetics in the presence of mixtures of diluents are rarely reported. This report describes the curing behavior of VERs in the presence of a mixture of styrene and methyl methacrylate (MMA; 40% w/w) as the reactive diluent. The curing results are also compared with those of VER cured in the presence of styrene or MMA alone.

EXPERIMENTAL

Bisphenol-A-based epoxy resin (EPG-280; SIP Resins, Madras, India; epoxide equivalent weight of 190 as determined by the pyridinium chloride method¹², acrylic acid (Fluka Chemie, Germany), tributyl amine (SD's), benzoyl peroxide (SD, India), styrene (Ranbaxy, India), and methyl methacrylate (MMA; Robert Johnson, India) were used in this study. Styrene and MMA were purified according to the standard procedures.^{13,14}

VER was prepared with a 1:0.9 mole ratio of bisphenol-A epoxy and acrylic acid in the presence of tributyl amine as catalyst (1 phr by weight of the epoxy resin). The reaction was carried out at 90 ± 2°C until the VER of the desired acid value (~6 mg of KOH per gram of solid), as determined by the method of Ogg et al.,¹⁵ was obtained. The progress of the reaction was monitored by determining the acid number of the reaction mass every 30 min. The extent of reaction and number average degree of polymerization were calculated using Carother's equation. The light-colored transparent VER thus prepared was cooled and stored in a refrigerator at ≈10°C to prevent further reactions.

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TABLE I
Samples and their Corresponding Weight Fractions

Diluent	Percent weight fraction				
	V _A	V _B	V _C	V _D	V _E
Styrene	40	30	20	10	0
MMA	0	10	20	30	40

Five samples were prepared by mixing the VER, diluent(s), and benzoyl peroxide (2 phr) at 30°C until the mixture became homogeneous. The samples were prepared just before taking the dynamic DSC scans, and the details are given in Table I.

A thermal analyzer (Thermal Analyzer 2000; TA Instruments) equipped with a differential scanning calorimeter (DSC; 2910 Differential Scanning Calorimeter) was used to study the curing behavior of resins. Scans were obtained under dynamic conditions with program rates of 2, 5, 10, 15, and 20°C min⁻¹ from 40°C to the temperature at which the exothermic reactions were complete. The activation energy E (within ±3% accuracy) was calculated from the DSC scans by the Ozawa method.¹⁶ This method assumes that the extent of reaction at the peak exotherm temperature is constant and independent of the programme rate:

$$E \cong 2.19R \frac{d \log \beta}{d(1/T)} \quad (1)$$

where R is the gas constant, β is the program rate, and T is the peak temperature. Further refinements of E values were carried out by iteration until the two successive values were almost identical.

The frequency factor, Z , was calculated using Kissinger's equation:¹⁷

$$Z (\text{min}^{-1}) = \frac{\beta E e^{E/RT}}{RT^2} \quad (2)$$

The specific rate constant, K_T , was calculated using the Arrhenius equation:

$$K_T = Z e^{-E/RT} \quad (3)$$

RESULTS AND DISCUSSION

The prepared resin was characterized by Fourier transform infrared (FTIR) spectroscopy.^{18,19} Typical dynamic DSC scans for the curing of all the five samples (V_A-V_E) at the program rate of 10°C min⁻¹ are shown in Figure 1. The exothermic curves are in the temperature range 86–153°C. The DSC scans of V_A-V_E at other program rates of 2, 5, 15, and 20°C min⁻¹ also showed a similar trend, except for the range of exothermic reactions. The thermogram of V_A shows that the rate of curing becomes sluggish in the later stages

of reaction and it is comparatively faster in the early stages, whereas the thermogram of V_E shows the opposite behavior. However, the nature of the thermograms of V_B, V_C, and V_D is different than that of V_A and V_E and is more close to that of the monomer, which has been used in the higher proportion. The difference in the nature of exotherms containing styrene, MMA, and their mixtures is due to differences in their polar characteristics. In the presence of MMA (electron acceptor), the reactivity of tributyl amine (electron donor) present in the system is enhanced and it acts as a chain transfer agent.²⁰ The reaction mechanism is shown in Scheme 1.

The growing MMA chains, being electron acceptors in nature, abstract hydrogen radicals from the tertiary amines and get terminated, leaving the tertiary amine free radical, which can further terminate another chain.²¹ The tertiary amine, acting as a chain transfer agent in the presence of MMA, may be the reason for its delayed curing with vinyl ester in the initial stages, whereas its effect is not possible in the later stages of the reaction.

The onset temperature of curing (T_o), the exothermic peak positions (T_p), and the final temperature of curing (T_f) were determined from the DSC scans obtained at every program rate and are given in Table II. It is apparent from the data that T_o and T_p , at every program rate, are lower for samples V_B, V_C, and V_D, which contain mixtures of styrene and MMA, than for samples V_A and V_E, which have only styrene or MMA alone as a diluent. This result indicates that mixtures of styrene and MMA as diluent are more reactive in

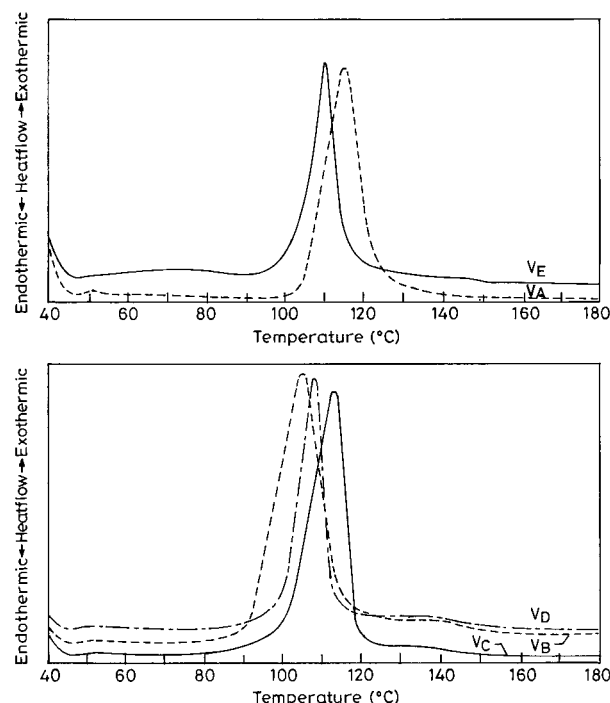
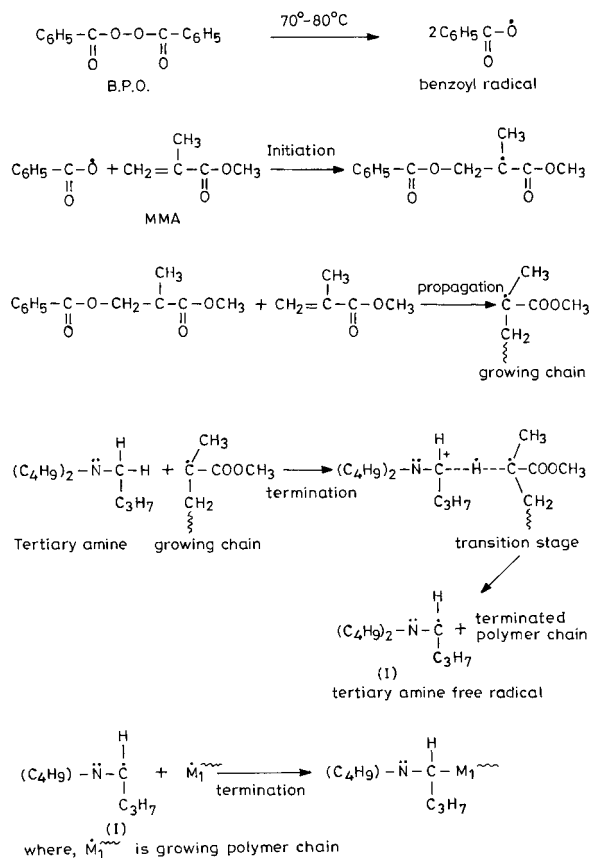
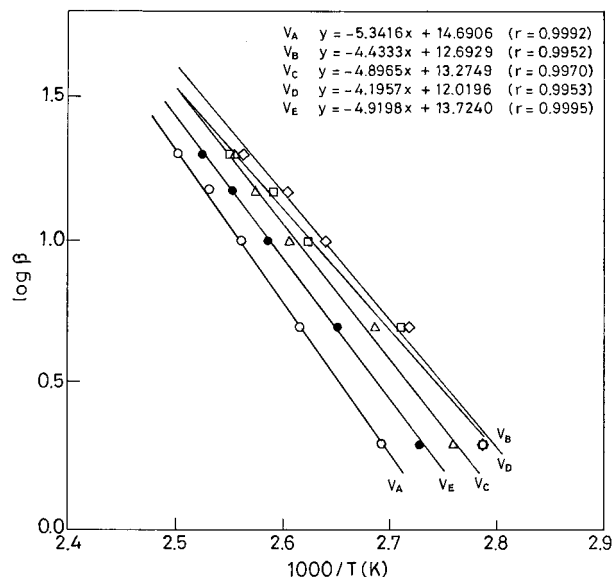


Figure 1 Dynamic DSC scans of V_A-V_E at 10°C min⁻¹.



Scheme 1

Figure 2 Plots of $\log \beta$ versus the reciprocal of cure peak temperature for VEs.

curing VEs than styrene or MMA alone. The T_o and T_p are highest for V_A and lowest for V_D , indicating that the curing reaction starts early at any program rate when the mixtures of diluents are used.

Using the Ozawa method, $\log \beta$ was plotted against the reciprocal of the cure peak temperature (Figure 2), and the activation energy and frequency factor were

TABLE II
Curing Behavior of Vinyl Ester Resins Containing Styrene and MMA

Sample	Heating rate ($^\circ\text{C}$)	T_o ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	E (Kcal mol $^{-1}$)	Z (min $^{-1}$)
V_A	2	80.94	98.32	120.32	22.90	4.91×10^{12}
	5	89.31	109.15	135.76	22.90	4.82×10^{12}
	10	107.01	116.65	148.80	22.90	5.21×10^{12}
	15	111.80	121.83	150.97	22.90	5.15×10^{12}
	20	116.23	125.75	155.40	22.90	5.05×10^{12}
V_B	2	76.29	85.67	115.60	18.80	3.99×10^{10}
	5	82.65	94.82	119.68	18.80	4.97×10^{10}
	10	89.23	105.60	151.50	18.80	4.54×10^{10}
	15	96.45	110.85	143.39	18.80	6.58×10^{10}
	20	105.22	117.10	147.80	18.80	4.20×10^{10}
V_C	2	78.10	89.37	115.87	20.00	1.67×10^{11}
	5	83.34	99.16	128.64	20.00	1.92×10^{11}
	10	87.91	110.61	145.89	20.00	1.61×10^{11}
	15	99.31	115.39	148.56	20.00	1.70×10^{11}
	20	108.27	119.85	151.60	20.00	1.65×10^{11}
V_D	2	73.77	85.70	120.90	17.70	9.09×10^9
	5	79.44	95.85	128.98	17.70	9.74×10^9
	10	86.00	107.90	146.10	17.70	8.47×10^9
	15	96.32	112.81	150.45	17.70	9.22×10^9
	20	103.40	120.25	152.76	17.70	7.66×10^9
V_E	2	78.25	93.38	121.87	21.00	5.04×10^{11}
	5	84.20	104.10	130.78	21.00	5.22×10^{11}
	10	88.41	113.60	150.20	21.00	5.01×10^{11}
	15	105.88	118.70	150.89	21.00	5.16×10^{11}
	20	110.09	123.02	153.46	21.00	5.02×10^{11}

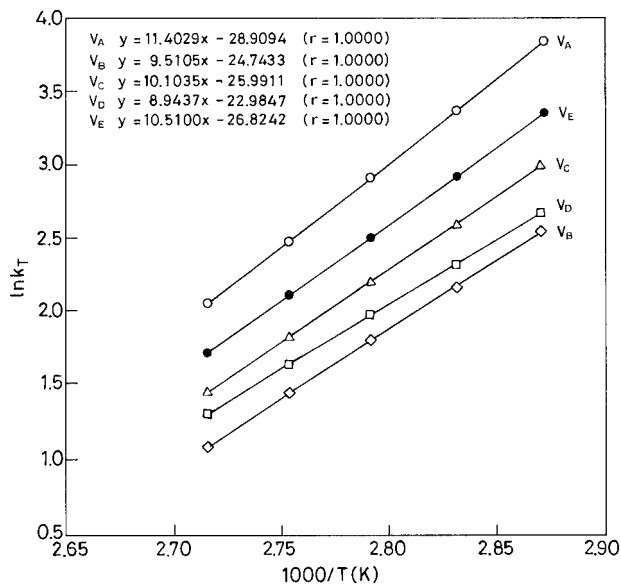


Figure 3 Plots of $\ln K_T$ versus the reciprocal of temperature for VERs.

calculated for samples V_A–V_E from the slope obtained by regression analysis. The values of E and Z are given in Table II. It is apparent from the data that E and Z values are lower for V_D and V_B than V_A, V_E, and V_C. This result confirms that mixtures of styrene and MMA used in a 1:3 or 3:1 ratio are more reactive to curing reactions. The values of Z for V_A–V_E at different program rates vary over a narrow range, which suggests that the curing reactions are first order.

The specific rate constants K_T were calculated for all samples and were plotted against the reciprocal of the temperature (Figure 3). It is apparent from the results in this figure that the curing reaction obeys the Arrhenius law.

CONCLUSIONS

The curing behavior of VERs studied in the presence of styrene, MMA, and their mixture as reactive di-

lucents was dependent on the nature and weight ratio of the monomers. The mixtures of styrene and MMA in 3:1 and 1:3 weight ratios were more reactive to VER. The curing reactions followed first-order kinetics and obeyed the Arrhenius rate expression.

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